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(54) Title: DIE ADHESIVE OR ENCAPSULANT OF EPOXY SILOXANE AND POLYEPOXY RESIN

(57) Abstract

A die–attach adhesive or encapsulant addressing the poor shelf life, high modulus and slow cure of epoxy resin compositions comprises a composition containing in addition to from about zero to 95 % by weight of a particulate filler and from about 5–100 % by weight of a base resin composed of from about 5 to 90 parts by weight of a polyepoxy resin, the presence of from about 10 to 95 parts by weight of a cycloaliphatic epoxy functional siloxane along with from about 0.1 to 3 parts by weight of an iodonium salt and from zero to about 3 parts by weight of a copper compound, optionally including from about 3 to 30 parts by weight of a toughener. The compositions are used in methods for die attachment, solder or polymer bump reinforcement and glob–top die encapsulation.

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DIE ADHESIVE OR ENCAPSULANT OF EPOXY SILOXANE AND POLYEPOXY RESIN

Cross-Reference to Related Application

This application is a continuation-in-part of our earlier, copending application Ser. No. 08/568,273 filed December 6, 1995.

Field of the Invention

The invention relates to rapidly curing epoxide compositions and processes for die-attach adhesives, polymer bumps, underfill encapsulants, and glob-top encapsulants. The compositions comprise a cycloaliphatic epoxy-functional siloxane, an epoxy resin, a diaryliodonium salt thermal initiator, or radiation sensitive initiator, fillers and, optionally, a copper compound.

Background of the Invention

Epoxy resins are widely used in many industrial applications. They are known for their excellent chemical and thermal resistance, good electrical and mechanical properties and for their adhesion to a wide variety of substrates. However, polymers derived from epoxy resins commonly have higher coefficients of thermal expansion (CTE's) than the substrates on which they are placed. Consequently, when the formulations are used as bonding or encapsulation agents, the mismatch between the coefficients of thermal expansion of the polymer and the substrate results in stress, which may cause

cracking and loss of adhesion between the epoxide and the substrates. When the substrate is an electronic device, circuit failure results. To circumvent this problem, epoxy resins are often filled with inorganic filler. Typical fillers include particulate silica, ground quartz, alumina and aluminum nitride. However, as the filler loading increases, the viscosity of the formulation increases correspondingly. This phenomenon presents severe restrictions on the potential use of resin formulations having high filler ratios since their high viscosities dramatically increase problems during applying and processing them.

If it were possible to avoid the high viscosities associated with high filler loadings, many additional applications would be immediately affected. High thermal and electrical conductivity, high hardness, high tensile strength and modulus, low shrinkage, and high density, which result from high filler loadings, would also render such materials attractive for four specific applications: die-attach adhesives, polymer bumps, underfill encapsulants, and glob-top encapsulants.

Polymer die-attach adhesives are used to bond a chip or die to a carrier or a circuit board. The die-attach adhesive provides mechanical, electrical and thermal contact between the die and the substrate. The substrate could be a leadframe, a package case, a single or multilayer ceramic, or an organic composite. Die-attach adhesives are sought to replace the expensive gold preform approach previously employed for plastic package applications. Known die-attach adhesives commonly consist of a

conductive metal, usually flakes of silver or gold, together with a curable resin, commonly an epoxy or cyanate ester resin. These materials are applied as highly viscous pastes and cured in an oven.

Similarly, a polymer bump is a means of replacing conventional lead-tin solder used to attach dies to the chip carrier or lead frame. Usually, the solder is in the form of small balls placed at specific interconnects around the die. The die is inverted, placed on the substrate and heat is applied to melt the solder, thereby providing both electrical and mechanical connection to the substrate. Polymer-based replacements for solder balls are called "polymer bumps." On heating in an oven, the polymer bump must flow to wet the pads and cure, providing the desired adhesive, electrical and mechanical functions.

Underfill encapsulation is a technique used to reinforce conventional solder bumps connecting the dies to the substrate. A liquid encapsulant comprising a polymer is dispensed along the perimeter of the dies and drawn by capillary action along the surface of the solder bump connection to the substrate of the assembled package. Upon oven curing the encapsulant solidifies and reinforces the solder joints.

Glob-top encapsulation involves dispensing a liquid polymeric material atop a die or chip positioned in a packaging substrate. The polymer is subsequently solidified by thermal curing which provides a protective coating on the die. Generally,

a coating between 0.15 and 3.75 mm is applied to the die, depending on the packaging application.

To succeed in these applications, a candidate material must meet the following requirements:

1. give full cure in 60 seconds or less at 200° C or below for adhesive applications, and in 60 minutes or less at 160° C or below for encapsulation applications;

2. possess a pot life greater than 24 hours at 25° C;

3. have a weight loss on cure of less than 2%;

4. have a viscosity suitable for automated dispensing;

5. exhibit no filler settling on storage at 25° C or at subzero temperatures;

6. have minimal resin bleed (i.e. bleed should be less than 0.125 mm on a variety of substrates);

7. possess low to moderate die and/or substrate warpage after cure;

8. have a low moisture absorption (less than 0.5%) at room temperature (25° C) or at elevated temperatures (≥ 85° C); and

9. have excellent adhesion to various inorganic, organic, or metal substrates including solders, solder-masks, and fluxes.

Considerable effort has been expended by the electronics industry to produce a material that meets the above requirements for adhesive, polymer bump, and/or encapsulant applications. Epoxy resins, typically filled with 60-80% of an electrically conductive filler such as particulate silver or gold, have been proposed for die-attach adhesives.

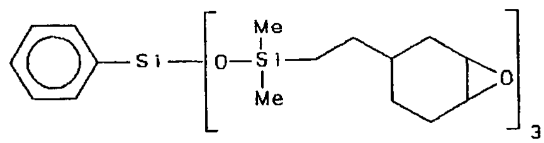
Likewise, epoxy resins, typically filled with 60-80% of an electrically nonconductive particulate filler such as silica, have been proposed for underfill and glob-top encapsulants. These epoxy-based materials appear to be suitable as adhesives or encapsulants because of their chemical resistance, electrical properties, thermal stability, and processability. However, from a polymeric materials standpoint, many of the aforementioned properties are interdependent, and one property of the system cannot be enhanced without altering another. In addition, epoxies tend to exhibit a poor shelf life, high modulus, and slow cure under normal curing conditions. Therefore, due to the aforementioned problems and disadvantages, no epoxy-based materials are currently available that meet all the above-listed requirements for die-attach adhesives, polymer bumps, underfill, and/or glob-top encapsulants.

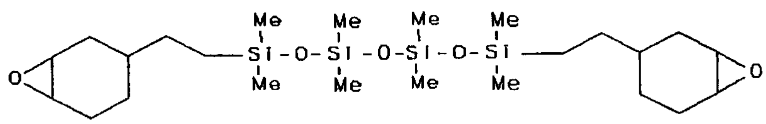
Summary of the Invention

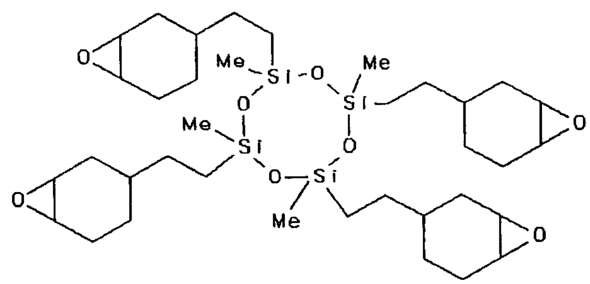
The present invention is addressed to superior, epoxy formulations useful as die-attach adhesives (die bonding agents), polymer bumps, underfill, or glob-top encapsulants.

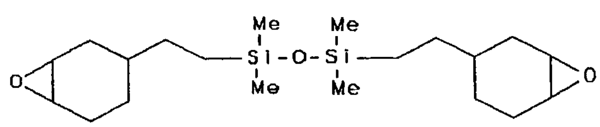
In one aspect the invention relates to resin compositions comprising from about 5 to 100% by weight of a base resin and from about zero to 95% by weight of a particulate filler, wherein the base resin comprises:

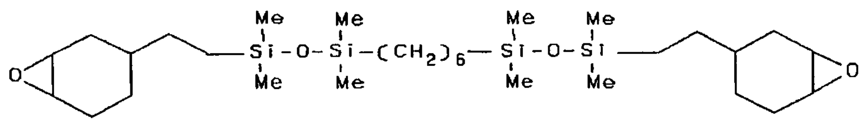
(a) from about 10 to 95 parts by weight of a cycloaliphatic epoxy functional siloxane selected from the group comprising

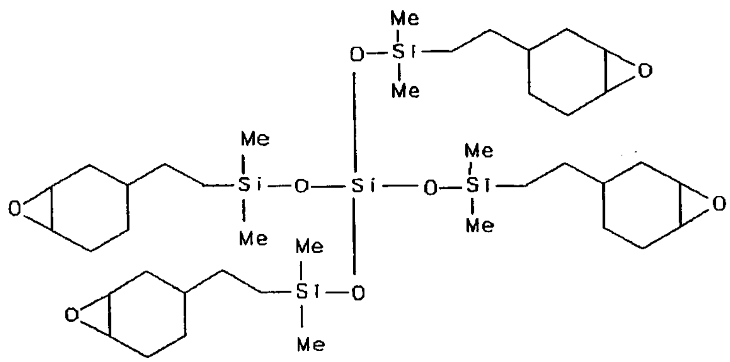






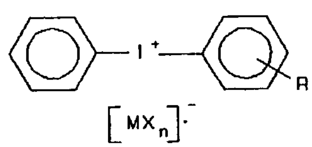






(b) from about 5 to 90 parts by weight of a non-silicon-containing di-, tri-, or polyepoxy resin or mixture of such resins;

(c) from about 0.1 to 3 parts by weight of an iodonium salt of formula



wherein M is selected from the group comprising boron, phosphorus, and antimony; X is halogen; n is 4 or 6; and R is selected from the group comprising hydrogen, C_1 to C_{20} alkyl, C_1 to C_{20} alkoxyl, C_1 to C_{20} hydroxyalkoxyl, halogen, and nitro; and

(d) from zero to about 3 parts by weight of a copper compound selected from the group comprising copper stearate, copper naphthenate, copper acetate, copper acetylacetonate, and copper 1,3-pentadienoate.

Preferably, the resin composition will contain from about 5 to 70% by weight of the base resin and from about 30 to 95% by weight of the particulate filler. The particulate filler may be a conductive metal, such as silver or gold, or it may be an electrically nonconductive material, such as silica, quartz, alumina, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, boron nitride, carbon black, diatomaceous earth, etc. The non-silicon-containing di-, tri-, or polyepoxy resin may be a cycloaliphatic resin, particularly 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate, dicyclopentadiene dioxide, or bis(3,4-epoxycyclohexyl adipate; a resin of diglycidyl ether of bisphenol A; a resin of diglycidyl ether of bisphenol F; a resin of diglycidyl ether of brominated bisphenol A; an epoxidized vegetable oil; an epoxy cresol novolac; an epoxy phenol novolac; or an α-olefin epoxide. A preferred iodonium salt is [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate.

The composition may additionally comprise (a) from about 3 to 30 parts by weight of a toughener selected from the group comprising epoxidized polybutadiene, carboxyl-terminated polybutadiene, carboxyl-terminated polybutadiene acrylonitrile, and particulate elastomer fillers; (b) from about 0.5 to

8 parts by weight of an adhesion promoting agent selected from the group comprising glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, and mixtures thereof; or a combination of any of (a) and (b).

A particularly preferred resin composition, especially useful as a die-attach adhesive, comprises from about 5 to 40% by weight of the base resin and from about 60 to 95% by weight of the particulate filler selected from the group comprising silver, gold, silica, alumina, quartz, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride. In this embodiment, the base resin comprises: (a) from about 20 to 45 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl) ethyl] disiloxane; (b) from about 40 to 60 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate; (c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; (d) from zero to about 2 parts by weight of copper stearate or copper naphthenate; (e) from about 0.4 to 3.5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and (f) from about 5 to 20 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

Another particularly preferred resin composition, especially useful as a polymer bump or solder bump replacement, comprises from about 5 to

40% by weight of the base resin and from about 60 to 95% by weight of an electrically conductive particulate filler such as silver or gold. In this embodiment, the base resin comprises: (a) from about 20 to 50 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane; (b) from about 30 to 60 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate; (c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; (d) from zero to about 0.3 parts by weight of copper stearate or copper naphthenate; (e) from about 1 to 5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and (f) from about 5 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

Another particularly preferred resin composition, especially useful as an underfill encapsulant, comprises from about 30 to 50% by weight of the base resin and from about 50 to 80% by weight of an electrically nonconductive particulate filler selected from the group of silica, quartz, alumina, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride. In this composition, the base resin comprises: (a) from about 30 to 70 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane; (b) from about 20 to 65 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate; (c) from about 0.5 to 3 parts by weight

of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; (d) from zero to about 1.5 parts by weight of copper stearate or copper naphthenate; (e) from about 1 to 8 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and (f) from about 3 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

Another particularly preferred resin composition, especially useful as a glob-top encapsulant, comprises from about 15 to 40% by weight of the base resin and from about 60 to 85% by weight of an electrically nonconductive particulate filler selected from the group comprising silica, quartz, alumina, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride. The base resin comprises: (a) from about 20 to 50 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane; (b) from about 30 to 70 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate and from zero to about 30 parts by weight of a diglycidyl ether of bisphenol A, a diglycidyl ether of bisphenol F, a diglycidyl ether of tetrabromo-bisphenol A, an epoxy cresol novolac, or an epoxy phenol novolac; (c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; (d) from zero to about 1 part by weight of copper stearate or copper naphthenate; (e) from about 1 to 5 parts by weight of glycidoxypropyltrimethoxysilane,

octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and (f) from about 4 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

In another aspect, the invention relates to a method for attaching a die to a substrate comprising: (a) depositing on a substrate a die-attach adhesive comprising a resin composition as described above; (b) positioning a die on the substrate in contact with the die-attach adhesive composition; and (c) heating the substrate, die and die-attach adhesive at 110° to 200°C for 0.5 to 240 minutes. The person of skill will, of course, appreciate that depositing the composition on the die would be equivalent to depositing it on the substrate for the purpose of the invention. Preferably, the heating step is performed at 130 to 150°C for 30 to 90 minutes; at 150 to 160°C for 5 minutes to 1 hour; or at 160 to 180°C for 30 seconds to 5 minutes.

In yet another aspect, the invention is a method for reinforcing a solder bump connection or a polymer bump connection from a die to a substrate comprising: (a) depositing an underfill encapsulant comprising a resin composition as described above on the periphery of a die, wherein the die is both physically and electrically connected to a substrate by a solder bump connection or a polymer bump connection; (b) allowing the deposited underfill encapsulant composition to contact the substrate while simultaneously contacting the die through capillary action along the surface of the solder or polymer bump connection; and (c) heating the substrate, die

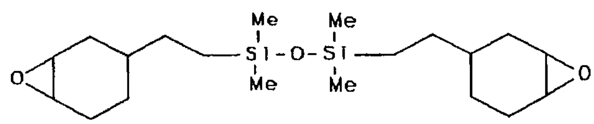
and underfill encapsulant at 100 to 170°C for 5 to 240 minutes, preferably at 120 to 160°C for 15 to 180 minutes. The underfill encapsulant is deposited to a thickness between about 0.025 and 1 mm, but a thickness between about 0.025 and 0.1 mm is preferred.

In yet another aspect, the invention is a method for protecting a die attached to a substrate comprising: (a) depositing a glob-top encapsulant comprising a resin composition as described above atop a die attached to a substrate; and (b) heating the die and glob-top encapsulant at 100 to 170°C for 5 to 240 minutes, preferably at 120 to 160°C for 15 to 180 minutes. Typically the composition is dispensed onto the die to a thickness between about 0.10 and 1.25 mm thick depending on the packaging application.

Even at a filler loading up to 95% for higher thermal and electrical conductivity, the viscosities of the compositions are still low enough for dispensing and other application conditions. The compositions also possess high thermal and electrical conductivity, high hardness, low water absorption, and low shrinkage. In addition, these compositions can be cured rapidly at low temperatures and yet provide an extended shelf life at room temperature. The above-mentioned combination of properties of the polymer together with low viscosity and rapid curing times of the prepolymer mix have not previously been achieved with single component epoxy resin formulations.

Detailed Description of the Invention

Shown below are the structures of several cycloaliphatic epoxy functional siloxane resins that may be included in the base resin component of the resin composition of the present invention:



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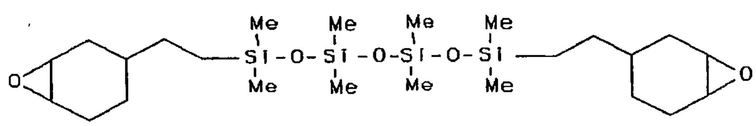

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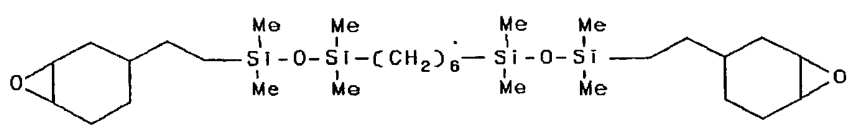

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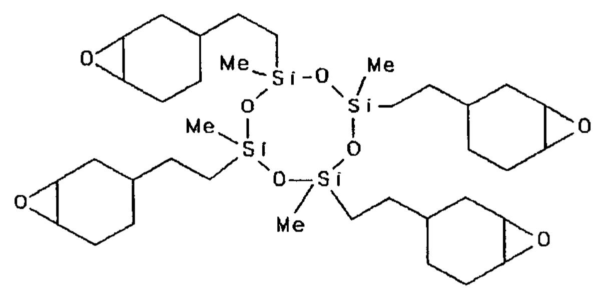

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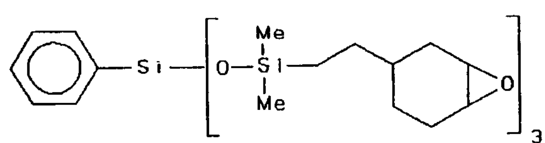

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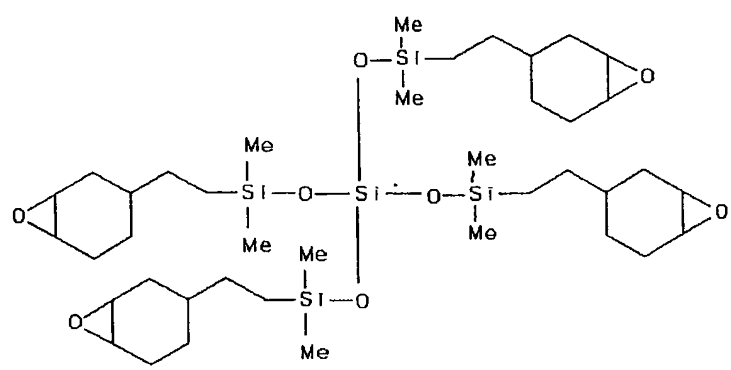
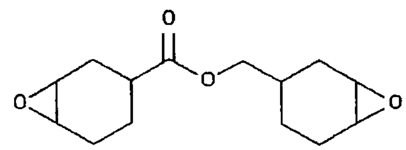


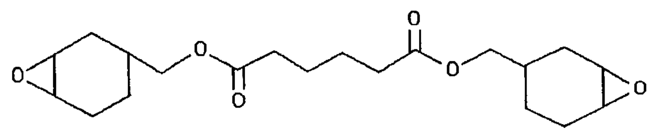
VI

Structure I in the above list, 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane, is referred to in this disclosure as "siloxy monomer I." Cycloaliphatic epoxy functional siloxane resins can be incorporated into the final formulation in amounts ranging from about 10 to 95% of the total epoxy base resin. The term "cycloaliphatic epoxy" as used herein refers to epoxy resins in which the reactive epoxide functionality is attached to a 5, 6 or 7-membered ring so as to form an oxabicyclo[n.1.0]alkane, where n is 5, 6 or 7.

A wide variety of other non-silicon containing epoxy resins may be used in combination with the above cycloaliphatic epoxy functional siloxane resins in the base resin. These include cycloaliphatic epoxy resins such as 3,4-epoxycyclohexyl 3',4'-epoxycyclohexane carboxylate (EECH), bis(3,4-epoxycyclohexyl) adipate, 4-vinylcyclohexene dioxide, limonene dioxide and dicyclopentadiene dioxide; α-olefin epoxides such as 1,2-epoxytetradecane, 1,2-epoxydecane, 1,2-epoxydodecane; glycidyl ethers including bisphenol-A diglycidyl ether, bisphenol-F diglycidyl ether, and their extended chain analogs, 1,4-butanediol diglycidyl ether; brominated epoxy resins such as diglycidyl ethers of tetrabromo-bisphenol-A; epoxy cresol novolacs; epoxy phenol novolacs; epoxidized vegetable oils such as epoxidized soybean oil and epoxidized linseed oil; and glycidyl ester resins, as for example, diglycidyl phthalate to mention a few. 3,4-Epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate, also known as 7-oxabicyclo[4.1.0]hept-3-ylmethyl 7-oxabicyclo[4.1.0]heptane-3-carboxylate)

EECH 

which is available from Union Carbide as ERL 4221E, bis(3,4-epoxycyclohexyl) adipate

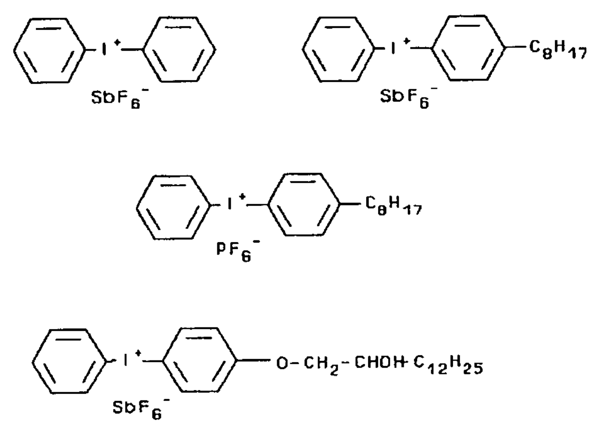


which is available from Union Carbide as ERL 4299, and dicyclopentadiene dioxide are the preferred cycloaliphatic epoxy resins. The above listed non-silicon containing epoxy resins may be included alone with the cycloaliphatic epoxy functional siloxane to form a binary epoxy mixture or further combined with others to make more complex epoxy mixtures.

The epoxy formulations of the invention undergo rapid and efficient cure at low temperatures through the addition of a diaryliodonium salt catalyst to the base resin. The general structure of a diaryliodonium salt is represented as

$$Ar\text{-}I^{+}\text{-}Ar \quad X^{-}$$

in which Ar represents an aryl group and X^- is a complex anion of the type BF_4^-, PF_6^-, PF_6^-, $CF_3SO_3^-$, and $(C_6F_5)_4B^-$. Some examples of diaryliodonium salts which may be employed in this invention include the following:



Of the diaryliodonium salt examples shown above, [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate, is preferred. Typically, the base resin comprises from about 0.1 to 3 parts by weight by weight of the diaryliodonium salt.

A copper compound may optionally be employed as a co-catalyst in the base resin to provide for thermal curing of the epoxy resin at lower temperatures. For example, as shown in the following Example 3, the addition of a copper compound to the base resin of Example 2 halves the gel time at 140° C. However, the presence of the copper compound often decreases the shelf life of the epoxy formulations. Thus, the artisan will normally decide whether to include the copper compound depending on the relative importance of shelf life and cure time for the particular application. Copper compounds which may be used as co-catalysts in the course of this invention include almost any copper compound known; however, those which exhibit reasonable

solubility in the epoxy resin are preferred: copper stearate, copper naphthenate, copper acetate, copper acetylacetonate, copper 1,3-pentadienoate, etc. The base resin may include up to about 3 parts by weight of the copper compound. However, typically, only about 7 to 15% by weight of the amount of the iodonium salt catalyst included in the base resin is required to cure the epoxide resin.

A wide range of thermal and electrical conducting and nonconducting fillers may be employed together with the epoxy resins cited above in the base resin for the formulation of a die-attach adhesive, polymer bump, underfill encapsulant, or glob-top encapsulant. These include, but are not limited to, particulate silica, ground α-quartz, alumina, aluminum nitride (preferably coated with silica), barium sulfate, alumina trihydrate, boron nitride, flaked or particulate silver, flaked or particulate gold, glass microballoons, silver plated microballoons, silver plated glass beads, carbon black, and diatomaceous earth. A preferred electrical conducting filler is silver of particle size between 1 and 35 μm. Preferred electrical nonconducting fillers, particularly useful in underfill and glob-top applications, include silica and aluminum nitride (preferably coated with silica) having particle sizes between 0.5 to 120 μm. The filler content can range from 10 to 95% by weight of the final formulation depending on the application. Typically, die-attach adhesives will contain from about 30 to 95% by weight particulate filler; polymer bumps, from about 60 to 95% by weight of an electrical conducting filler; underfill encapsulants, from about 50 to 80% by weight of an electrical

nonconducting filler; and glob-top encapsulants, from about 60 to 85% by weight of an electrical nonconducting filler.

Aluminum nitride and silica fillers may be treated with silane using commonly known methods, or obtained commercially, then added to the composition as electrically nonconductive fillers. Examples of commercially available silane-treated fillers include spherical silica treated with octyltriethoxysilane or glycidoxypropyltrimethoxysilane from Tatsumori as PLV-6S or PLV-10S. Note that no particular advantage is observed with the use of treated as opposed to untreated silica or with the use of spherical as opposed to particulate silica. Therefore, any of the aforementioned silica variations may be employed.

Aluminum nitride, also useful as an electrically nonconductive, but thermally conductive, filler in the formulation, is preferably coated with silica because of the superior hydrolytic stability the coated material has over uncoated aluminum nitride, i.e. hydrolysis of the nitride to ammonia is avoided upon contact with water if a coating of silica is deposed on the nitride. In addition, the inclusion of silica-coated aluminum nitride to the formulation is advantageous because a higher thermal conductivity can be obtained with the coated aluminum nitride than with crystalline silica alone. A suitable silica-coated aluminum nitride for use in the formulation and its respective method of preparation are disclosed in U.S. Pat. Nos. 5,508,110 and 5,234,712. Commercially, the material is available from Dow Chemical Company as Dow Filler Grade AlN.

The resin formulations of the present invention may be modified by the incorporation of hydroxy or other functional oligomers to provide flexible resins. To this end, hydroxyl terminal polyesters, epoxidized polybutadiene, polyether polyols, and the condensation products of carboxylated butadiene or carboxylated butadiene acrylonitrile with epoxides can be employed. Formulations can be further modified by adding reactive particulate rubber fillers or polymeric rubber modifiers to improve the toughness of the compositions. Other modifiers, such as wetting, flow control, coupling and flatting agents, as well as fire retardants, pigments and dyes such as carbon black and phthalo blue, may also be incorporated in the formulations of this disclosure.

Although the basic compositions exhibit the desired features for die-attaches, polymer bumps, underfill encapsulants, and glob-top encapsulants, it has been found that they can be optimized for use in specific IC fabrication processes by the inclusion of certain additives. To improve the survival of the polymeric die-attach or encapsulant on further processing at high temperatures, it is advantageous to add from about 3 to about 30 parts by weight of a toughener to the base resin. Epoxidized polybutadiene of molecular weight 1500-3000 having an oxygen content of about 6% (available from Sartomer as [PolyBD]™ and from ELF Atochem) and carboxyl-terminated polybutadiene or carboxyl-terminated polybutadiene acrylonitrile of molecular weight 3000-5000 (available as HYCAR™ CTB-2000-162 and CTBN 1300 x 31, respectively, from B.F. Goodrich) have been found suitable for this purpose. Antioxidants may be added to improve storage life. Blocked phenols, such

as Ciba-Geigy's IRGANOX™ have been found suitable for this purpose. Surfactants, such as Pluronic L-101 which is commercially available from BASF, may also be added to improve flow and wetting characteristics. Concentrations from about 0.1 to 2.0 parts by weight based on the base resin have been found suitable for this purpose.

The resin compositions of the present invention can be cured by application of thermal energy; the cure may be conducted in an oven, on a hot plate, under infrared radiation or under microwave irradiation. Heating may be varied according to time and temperature so as to provide the optimal combination of time and temperature for the specific application.

The resin compositions of the present invention may be deposited onto a substrate to attach a die to a substrate (die-attach adhesive), onto the periphery of a die connected to a substrate by a solder bump or polymer bump to reinforce the solder or polymer bump connection (underfill encapsulant), or onto a die attached to a substrate to protect the die (glob-top encapsulant). The compositions may be deposited by screen printing, stencil printing, syringe dispensing or any of the other techniques well known in the art. Typical die-attach adhesives based on the above formulations are cured at temperatures from about 110 to 200° C. Cure times can range from 30 seconds to 2 hours. Typical underfill or glob-top encapsulants are cured at temperatures from 100 to 170° C for 5 minutes to 2 hours, but preferably from 120 to 160° C for 15 to 180 minutes.

Thus, for example, for use as a die-attach adhesive, the resin composition preferably comprises from about 5 to 40% by weight base resin and from about 60 to 95% by weight particulate filler, thermally conducting and either electrically conducting or nonconducting. The base resin preferably comprises (a) from about 20 to 45 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl]disiloxane; (b) from about 40 to 60 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate; (c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)phenyl] phenyl iodonium hexafluoroantimonate; (d) from zero to about 2 parts by weight of copper stearate or copper naphthenate; (e) from about 0.4 to 3.5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or combinations thereof; (f) from about 3 to 15 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile. The above die-attach adhesive is initially deposited on a substrate, and a die is positioned on the substrate in contact with the adhesive. Curing may be accomplished at 110 to 200° C for 0.5 to 240 minutes. Alternatively, the die-attach adhesive can be cured at 130° to 150° C for 30 to 90 minutes, at 150° to 160° C for 5 minutes to 1 hour, or at 160° to 180°C for 30 seconds to 5 minutes. Likewise, based on the description provided above, one skilled in the art can optimize the resin composition of the present invention and optimize the heating times and temperatures of the method of the present invention for applications related to underfill and glob-top encapsulation.

The following examples are given by way of illustration and are not intended to be limitative.

EXAMPLE 1- DIE ATTACH ADHESIVE

A base formulation consisting of the following components was prepared:

Component	Parts by Weight
EECH cycloaliphatic epoxy resin (ERL 4221E)	50
Siloxy monomer I	37
Epoxidized polybutadiene (PolyBD 565)	10
4(2-hydroxy-1-tetradecyloxyphenyl) phenyliodonium hexafluoroantimonate	1.0
Copper stearate (10% dispersion in Epon 828)	1.1
Antioxidant (Irganox 1035)	0.3
Adhesion promoter - glycidyloxypropyltrimethoxysilane (A187)	0.7
Wetting agent (Pluronic L-101)	0.1

Using the above base resin, three formulations with particulate silver were prepared containing the following two particulate silver materials (Silflake 95-235, 3-5μm and Silflake 95-131, 5-9μm).

Formulation 1-1

Base resin	19
Silflake 95-235	40.5
Silflake 95-131	40.5

Formulation 1-2

Base resin	19
Silflake 95-235	81

Formulation 1-3

Base resin	17
Silver flake 95-235	83

The following table gives the viscosity, glass transition temperature and the gel times at 140 and 175° C.

Property	Formulation 1	Formulation 2	Formulation 3
Visc., cps at 25°C (Cp-52, 2.5 rpm)	15000	21000	28000
T_g, °C	>150	>150	>150
Gel Time (min) 140° C 175° C	 2 <1	 2 <1	 2 <1

Formulation 1-1 was further tested and the following properties were observed following a cure cycle of 1 hour at 140° C.

<u>Specific Gravity</u>	3.74
<u>Coefficient of thermal expansion</u>	45-55 ppm

Storage Modulus	@ 25° C	8±1 GPA
	@ 150° C	0.9±0.1 GPA
Shear Strength, psi		>2000
Die-Shear, Kg (1.25 mm X 1.25 mm, bare copper) Cure 1 min @ 170°C		>3.00
Ionic Content	(Na,K,Cl)	<10 ppm
Maximum Weight loss during cure		
	@140° C	<0.05%
	@160° C	<0.1%
Resin Bleed		0 to 0.075 mm
Die Warpage		low to no die warpage
Silver settling		none
Shelf life		
	@ 25° C	>14 da
	@ -10° C	>3 mo
	@ -40° C	>6 mo
Weight loss (Thermal Stability)		
	@ 300° C	<0.15%
	@ 350° C	<0.3%
	@ 425° C	<1.0%
Moisture Absorption		
	7 days at 25°C	0.05%
	85°C / 85% R.H.	0.15%

EXAMPLE 2-DIE ATTACH ADHESIVE

In a similar manner to Example 1, a base resin was prepared consisting of the following components:

Component	Parts by Weight
ERL 4221E (EECH)	46
Siloxy monomer I	36
Siloxy monomer/carboxyl terminated polybutadiene adduct (50:50)	15
Irganox 1035	0.3
4(2-hydroxy-1-tetradecyloxyphenyl)phenyl-iodonium hexafluoroantimonate (50% in 4221E)	2.0
A187 glycidyloxypropyltrimethoxysilane	0.7
Pluronic L-101 surfactant	0.1

Using the above base resin, a formulation 2-1 with particulate silver was prepared containing the following components:

Base resin	19
Silflake 95-235	40.5
Silflake 95-131	40.5

The above formulation had a viscosity of 15000 centipoise at 25° C. The gel time obtained on curing at 140° C was 4 minutes. At 175° C the gel time was less than 1 minute and the polymer so obtained had a T_g of >150° C.

EXAMPLE 3-DIE ATTACH ADHESIVE

In a similar manner to Example 2, a base resin was prepared consisting of the following components:

Component	Parts by Weight
ERL 4221E (EECH)	46
Siloxy monomer I	35
Siloxy monomer/carboxyl terminated polybutadiene adduct (50:50)	15
Irganox 1035	0.3
4(2-hydroxy-1-tetradecyloxyphenyl)phenyl-iodonium hexafluoroantimonate (50% in 4221E)	2.0
A187 glycidyloxypropyltrimethoxysilane	0.7
Pluronic L-101 surfactant	0.1
Copper stearate (10% dispersion in Epon 828)	1.1

Using the above base resin, a formulation 3-1 with particulate silver was prepared containing the following components:

Base resin	19
Silflake 95-235	40.5
Silflake 95-131	40.5

The above formulation had a viscosity of 16000 centipoise at 25° C. The gel time obtained on curing at 140° C was 2 minutes and at 175° C the gel time was <1 minute and the polymer so obtained had a T_g of >150° C. From this experiment, the effect of the presence of the copper stearate co-catalyst on shortening the cure time at 140° C can be seen.

EXAMPLE 4-DIE ATTACH ADHESIVE

Repeating the above procedure, a base resin was prepared consisting of the following components:

Component	Parts by Weight
ERL 4221E (EECH)	54
Siloxy monomer I	28
Epoxidized polybutadiene	15
4(2-hydroxy-1-tetradecyloxyphenyl)phenyl-iodonium hexafluoroantimonate	1.0
A187 glycidyloxypropyltrimethoxysilane	1.0
Copper stearate (10%) dispersion in Epon 828)	1.0

Using the above base resin, a formulation 4-1 with particulate silver was prepared containing the following components:

Base resin	21
Silflake 95-235	39.5
Silflake 95-131	39.5

The above formulation had a viscosity of 30000 centipoise at 25° C. After curing for 1 hour at 140° C, the polymer so obtained had a T_g of >140° C.

EXAMPLE 5-DIE ATTACH ADHESIVE

The above example was repeated with the following modifications. A base resin was prepared consisting of the following components.

Component	Parts by Weight
ERL 4221E (EECH)	49
Siloxy monomer I	25
Epoxidized PolyBD	15
α-olefin oxide	8.0
Irganox 1035	0.3
4(2-hydroxy-1-tetradecyloxyphenyl)phenyl-iodonium hexafluoroantimonate	1.0
A187 glycidyloxypropyltrimethoxysilane	0.7
L-101 nonionic surfactant	0.1
Copper stearate (10% dispersion in Epon 828)	1.0

Using the above base resin, a formulation 5-1 with particulate silver was prepared containing the following components:

Base resin	21
Silflake 95-235	39.5
Silflake 95-131	39.5

The above formulation had a viscosity of 13000 centipoise at 25° C. After curing for 1 hour at 140° C the T_g of the polymer so obtained was 120° C.

EXAMPLE 6-DIE ATTACH ADHESIVE

The above experiment was repeated with modifications. A base resin was prepared consisting of the following components:

Component	Parts by Weight
ERL 4221E (EECH)	50
Siloxy monomer I	27
Siloxy monomer/carboxyl terminated polybutadiene adduct (50:50)	12
α-olefin oxide	8
4(2-hydroxy-1-tetradecyloxyphenyl) phenyl-iodonium hexafluoroantimonate	1.0
A187 glycidyloxypropyltrimethoxysilane	0.7
Pluronic L-101 surfactant	0.1
Copper stearate (10% dispersion in ERL 4221)	1.0

Using the above base resin, a formulation 6-1 with particulate silver was prepared containing the following components:

Base resin	19
Silflake 95-235	40.5
Silflake 95-131	40.5

The above formulation had a viscosity of 18000 centipoise at 25° C. After curing for 1 hour at 140° C the T_g of the polymer so obtained was 130° C.

EXAMPLE 7 - DIE-ATTACH ADHESIVE

BASE FORMULATIONS	Parts by Weight
ERL 4221E	50
Siloxy Monomer	35
Siloxy: CTBN adduct (50:50)	15
Irganox 1035	0.3

FINAL FORMULATIONS	A	B	C
Base	21	21	11
Wetting Agent (Pluronic L-101)	0.2	0.2	0.2
Silane A-187	0.6	0.6	0.3
Silverflake AAR-0595	50	20	56
Silflake 450	28	58	32
Iod. Catalyst (50% in 4221 E)	0.55	0.55	0.4
Copper Naphthenate (8% Cu)	0.02	0.02	0.014

	A	B	C
Viscosity @ 25 °C, cps	8000	12000	25500
Gel Time @ 120 °C	-----2 mins-----		
Shelf Life @ 25 °C	-----> 7 days-----		
@-40 °C	-----> 6 months-----		
Cure Cycle	---1 hour @ 150 °C--- or ---1 min @ 170 °C---		
Cure Volatiles @ 150 °C	<0.2%	<0.2%	<0.1%
Volume Resistivity, ohm-cm	3.4×10^{-4}	4.8×10^{-4}	2.2×10^{-4}
Thermal Conductivity, w/m °C	>2	>2	>4

EXAMPLE 8

ELECTRICALLY NON-CONDUCTIVE DIE ATTACH ADHESIVE

In a similar manner to that of Example 2, a base resin was prepared consisting of the following components:

Component	Parts by Weight
ERL 4221E (EECH)	49
Siloxy monomer I	33
Siloxy monomer/carboxyl terminated polybutadiene adduct (50:50)	15
Irganox 1035	0.3
4(2-hydroxy-1-tetradecyloxyphenyl) phenyl-iodonium hexafluoroantimonate (50% in 4221E)	2.0
A187 glycidyloxypropyltrimethoxysilane	0.7
Copper stearate (10% dispersion in ERL 4221)	1.1

Using the above base resin, three formulations with various particulate fillers were prepared containing the following components:

Formulation 8-1

Base resin	25
Silica	75
Pluronic L-101	0.2

Formulation 8-2

Base resin	25
Silica-coated aluminum nitride (DOW)	75
Pluronic L-101	0.2

Formulation 8-3

Base resin	25
Calcined alumina	75
Pluronic L-101	0.2

Formulation 8-1 was further tested and the following properties were obtained:

Viscosity @ 25°C (cp-52, 5 rpm)	20,000 cps
Specific gravity	1.7
Gel time @ 140° C	1-2 mins.
Pot life @ 25° C	>14 days
Cure volatiles at 50° C	<0.05%
Glass transition temp. (T_g)	>150° C
Coefficient of thermal expansion (CTE)	16-19ppm
Hardness, Shore D	90-95
Storage Modulus	
@ 25° C	10GPA
@ 125° C	1 GPA
Wt. loss @ 300° C	<0.1%
Moisture absorption (7 days @ 25°C)	<0.15%
Die-Shear, Kg	>3.5
(1.25 mm X 1.25 mm, bare Copper) cure - 1 min @ 170°C	
Ionic content (Na, K, Cl)	<10 ppm
Shelf life @ 25° C	>14 days
@ -20° C	>3 months
@-40° C	>6 months

EXAMPLE 9 - UNDERFILL

	Parts by Weight		
BASE FORMULATIONS	A	B	C
ERL 4221E	50	50	47
Siloxy Monomer	37	37	35
Epoxidized PolyBD (Poly BD565)	10	x	x
Siloxy: CTB adduct (50:50)	x	10	15
Irganox 1035 (Antioxidant)	0.4	0.4	0.4
Silane A-187 (Adhesion promoter)	1.5	1.5	1.5
Copper Stearate (10% dispersion in Epon 828)	1.1	1.1	1.1

FINAL FORMULATIONS	A	B	C
Base	25.5	25.5	25.5
Wetting Agent (Pluronic L-101)	0.2	0.2	0.2
Silane Treated Silica	74.0	74.0	74.0
Iod. Catalyst: 4(2-hydroxy-1-tetradecyloxphenyl)phenyl-iodonium hexafluoroantimonate (50% in 4221E)	0.5	0.5	0.5

Viscosity @ 25 °C, cps	6,400	6,000	8,400
@ 80 °C, cps	425	380	510
Flow @ 80 °C, (0.05-0.075 mm gap between glass plates)			
5 minutes	<3.2 mm	<3.2 mm	<1.6 mm
10 minutes	<6.4 mm	<6.4 mm	<1.6 mm
Gel Time @ 80 °C	>20 mins	>20 mins	>20 mins
@ 120 °C	2 mins	2 mins	2 mins
CTE (0-100°C)	25 ppm	23 ppm	19 ppm
Tg	>140 °C	>140 °C	>140 °C

EXAMPLE 10 - UNDERFILL

	Parts by Weight	
BASE FORMULATIONS	A	B
ERL 4221E	50	51
Siloxy Monomer	38	39
Siloxy: CTB adduct (50:50)	10	8
Irganox 1035 (Antioxidant)	0.4	0.4
Silane A-187 (Adhesion promoter)	1.6	1.6

FINAL FORMULATIONS	A	B
Base	27.5	30.5
Triton X-100	x	0.7
Silane Treated Silica	72	68
Phthalo Blue (2% dispersion in 4221E)	0.4	0.4
Iod. Catalyst: (50% in 4221E)	0.55	0.61

Viscosity @ 25 °C, cps	5,500	3,600
@ 80 °C, cps	300	225
Flow @ 80 °C, (0.05-0.075 mm gap between glass plates)		
5 minutes	<3.2 mm	<9.5 mm
10 minutes	<6.4 mm	<12.7 mm
Gel Time @ 80 °C	>4 hours	>4 hours
@ 120 °C	5 - 7 mins	5 - 7 mins
Shelf Life @ 25 °C	>3 months	>3 months
@ -20 °C	>6 months	>6 months
@ -40 °C	>12 months	>12 months
CTE (0 - 100 °C)	25 ppm	29 ppm
Tg	>140 °C	>140 °C
Storage Modulus, GPA	8±1	6±1

EXAMPLE 11 - UNDERFILL

	Parts by Weight		
BASE FORMULATIONS	**A**	**B**	**C**
ERL 4221E	51	51	60
Siloxy Monomer	41	41	20
EPLO (Vikoflex 7190)	x	x	20
Siloxy: CTB adduct (50:50)	8	x	x
Epoxidized PolyBD (Poly BD605)	x	8	x
Irganox 1035 (Antioxidant)	0.4	0.4	0.4

FINAL FORMULATIONS	**A**	**B**	**C**
Base	29.5	29.5	30
Wetting Agent (Pluronic L-101)	1	1	x
Silane A-187 (Adhesion promoter)	1	1	1.4
Phthalo Blue dispersion	0.4	0.4	0.4
Silica (treated) PLV-6S	15	15	15
Silica, 4910-20	53	53	53
Iod. Catalyst (50% in 4221E)	0.7	0.7	0.7
Copper Naphthenate (8% Cu)	0.021	0.021	0.021
Mercaptopropyltriethoxysilane (A-1891)	1	1	1

Viscosity @ 25 °C, cps	7,100	6,600	9,100
@ 80 °C, cps	270	250	320
Flow @ 80 °C, (0.05-0.075 mm gap between glass plates)			
5 minutes	<6.4 mm	<12.7 mm	<12.7 mm
10 minutes	<12.7 mm	<19.1 mm	<19.1 mm
Gel Time @ 80 °C	>20 mins	>20 mins	>20 mins
@ 120 °C	2 mins	2 mins	2 mins
Shelf Life @ 25 °C	>7 days	>7 days	>7 days
@ -20 °C	>3 months	>3 months	>3 months
@ -40 °C	>6 months	>6 months	>6 months
Cure Cycle	-----------1 - 1 ½ hour @ 140 °C---------		
CTE (0 - 100°C)	27 ppm	30 ppm	33 ppm
Tg	>140 °C	>140 °C	>130 °C
Storage Modulus, GPA	7	7	7

EXAMPLE 12 - UNDERFILL

	Parts by Weight		
BASE FORMULATIONS	A	B	C
ERL 4221E	50	42	32
Siloxy Monomer	42	50	60
Epoxidized Poly-BD (Poly BD605)	x	4	x
EPLO/DCPDO Add.	8	4	8
Irganox 1035	0.4	0.4	0.4

FINAL FORMULATIONS	A	B	C
Base	30	30	31
Wetting Agent Pluronic (L-101)	1	1	1
Silane A-187 (Adhesion promoter)	0.5	0.5	0.5
Silane A-137	0.5	0.5	0.5
Phthalo Blue Dispersion (2%)	0.4	0.4	0.4
Silica (treated) PLV-6S	15	15	14
Silica, 4910-20	52	52	52
Iod. Catalyst (50% in 4221E)	0.7	0.7	0.7
Copper Naphthenate (8% Cu)	0.02	0.02	0.02

Viscosity @ 25 °C, cps	2,900	3,000	1,200
@ 80 °C, cps	200	175	95
Flow @ 80 °C, (0.05-0.075 mm gap between glass plates)			
5 minutes	25.4 mm	31.8 mm	38.1 mm
10 minutes	38.1 mm	44.5 mm	50.8 mm
Gel Time @ 80 °C	>20 mins	>20 mins	>20 mins
@ 120 °C	2 mins	2 mins	2 mins
Shelf Life @ 25 °C	>7 days	>7 days	>7 days
@ -20 °C	>6 months	>6 months	>6 months
@ -40 °C	>12 months	>12 months	>12 months
Cure Cycle	-----------1 - 1 ½ hour @ 140 °C-----------		
CTE (0 - 100°C)	45 ppm	30 ppm	35 ppm
Tg	>140 °C	>140 °C	>130 °C
Storage Modulus, GPA	6	6	6
Moisture Absorption (%) 14 days @ 85° C, 85% Relative Humidity	0.17	0.16	0.17

EXAMPLE 13 - UNDERFILL

	Parts by Weight	
BASE FORMULATIONS	A	B
ERL 4221E	30	20
Siloxy Monomer	60	66
Siloxy: CTBN adduct (50:50)	10	14
Irganox 1035	0.3	0.3

FINAL FORMULATIONS	A	B
Base	31	33
Wetting Agent (Pluronic L-101)	1	1
Silane A-187	0.5	0.5
Silane A-137	0.5	0.5
Silane A-1891	1	1
Phthalo Blue Dispersion (2%)	0.4	0.4
Silica PLV-65 (w/137)	14	13
Silica 4910-20	51	50
Iod. Cat. (50% in 4221E)	0.8	1.0
Copper Naphthenate (8% Cu)	0.022	0.022

	A	B
Viscosity @ 25 °C, cps	3,600	2,500
Flow @ 80 °C, (0.05-0.075 mm gap between glass plates)		
2 minutes	19.0 mm	12.7 mm
Gel Time @ 120 °C	------3-5 mins-------	
Shelf Life @ 25 °C	-------> 3 days------	
@ -40 °C	-------> 6 months----	
Cure Cycle	---1 hour @ 150 °C---	

EXAMPLE 14 - GLOB-TOP (HIGH PROFILE)

Parts by Weight

BASE FORMULATIONS	A	B	C
ERL 4221E	50	57	50
Siloxy Monomer	35	26	35
4221E: CTB adduct (50:50)	15	x	15
Siloxy: CTB adduct (50:50)	x	15	x
Irganox 1035	0.4	0.4	0.4

FINAL FORMULATIONS	A	B	C
Base	21.5	20.0	24.5
Wetting Agent (Pluronic L-101)	0.3	0.3	0.3
Silane A-187 (Adhesion promoter)	0.7	0.7	0.7
Carbon Black (Raven 450)	0.1	0.1	0.1
Treated Silica (FB74FCS)	77.0	78.5	74.0
Iod. Catalyst (50% in 4221E)	0.5	0.5	0.6
Copper Naphthenate (8% Cu)	0.016	0.016	0.2

Viscosity @ 25 °C, cps	60,000	67,000	25,000
Gel Time @ 120 °C	-----------------2 - 3 mins--------------		
Shelf Life @ 25 °C	----------------->7 days---------------		
@ -20 °C	----------------->6 months-----------		
@ -40 °C	----------------->12 months----------		
Cure Cycle	--------1 - 1 ½ hour @ 140 °C-------		
CTE (0 - 100°C)	12 ppm	13 ppm	18 ppm
Storage Modulus, @ 25 °C, GPA	15	15	10
Wt. Loss @ 300 C	-----------------<0.1%-----------------		
Moisture Absorption (14 days) @ 85 °C/85% Relative Humidity	-----------------<0.15%---------------		

EXAMPLE 15 - GLOB-TOP (LOW PROFILE)

BASE FORMULATIONS	Parts by Weight A	B
ERL 4221E	50	50
Siloxy Monomer	36	40
4221E: CTB adduct (50:50)	x	10
Siloxy: CTB adduct (50:50)	14	x
Irganox 1035	0.4	0.4

FINAL FORMULATIONS	A	B
Base	27.0	25.0
Wetting Agent (Pluronic L-101)	0.5	0.5
Silane A-187 (Adhesion promoter)	0.5	0.5
Phthalo Blue Disp.	0.2	0.4
Orasol Black CN	0.1	x
Treated Silica (FB74FCS)	32	33
Silica GP-3I	40	40
Iod. Catalyst (50% in 4221E)	0.6	0.6
Copper Naphthenate (8% Cu)	0.02	0.02

	A	B
Viscosity @ 25 °C, cps	30,000	20,000
Gel Time @ 120 °C	------------2 - 3 mins----------	
Shelf Life @ 25 °C	------------>7 days------------	
@ -20 °C	------------>6 months---------	
@ -40 °C	------------>12 months--------	
Cure Cycle	----1 - 1 ½ hour @ 140 °C---	
CTE (0 - 100°C)	19 ppm	20 ppm
Storage Modulus, @ 25 °C, GPA	9	8
Wt. Loss @ 300 C	------------<0.1%-------------	
Moisture Absorption (14 days) @ 85 °C/85% Relative Humidity	------------<0.15%------------	

EXAMPLE 16 - GLOB-TOP & DIE ATTACH ADHESIVES
(Thermally Conductive)

	Parts by Weight
BASE FORMULATIONS	
ERL 4221E	50
Siloxy Monomer	35
Siloxy: CTB adduct (50:50)	15
Irganox 1035	0.4

FINAL FORMULATIONS	A	B
Base	27.0	21.5
Wetting Agent (Pluronic L-101)	0.3	0.3
Silane A-187	0.7	0.7
Carbon Black (Raven 450)	0.1	0.1
Silica Coated Aluminum Nitride (DOW)	72	77
Iod. Catalyst (50% in 4221E)	0.6	0.5
Copper Naphthenate (8% Cu)	0.02	0.016
Mercaptopropyltriethoxysilane (A-1891)	1.0	1.0

	A	B
Viscosity @ 25 °C, cps	35,000	60,000
Gel Time @ 120 °C	------------2 mins--------------	
Shelf Life @ 25 °C	------------>7 days------------	
@ -20 °C	------------>6 months---------	
@ -40 °C	------------>12 months---------	
Cure Cycle	---------1 hour @ 140 °C-------	
CTE (0 - 100°C)	22 ppm	15 ppm
Storage Modulus, @ 25 °C, GPA	9	14
Wt. Loss @ 300 C	------------<0.1%------------	
Moisture Absorption (14 days) @ 85 °C/85% Relative Humidity	------------<0.15%------------	
Thermal Conductivity, W/Mk	>2.0	>2.5

EXAMPLE 17 - GLOB-TOP & DIE-ATTACH ADHESIVES
(Thermally Conductive)

BASE FORMULATIONS	Parts by Weight
ERL 4221E	50
Siloxy Monomer	35
Siloxy: CTBN adduct (50:50)	15
Irganox 1035	0.4

FINAL FORMULATIONS	A	B	C
Base	21	25	21
Wetting Agent (Pluronic L-101)	0.5	0.5	0.5
Silane A-187	0.7	0.7	0.7
Silica Coated AlN	78	74	76
Iod. Cat. (50% in 4221 E)	0.6	0.7	0.7
Copper Naphthenate (8% Cu)	0.02	0.02	0.02
Paraloid 2691*	-	-	3
Viscosity @ 25 °C, cps	80,000	20,000	90,000
Gel Time @ 120 °C	----------------2-4 mins----------------------		
Shelf Life @ 25 °C	----------------1-2 days----------------------		
@ -40 °C	---------------> 6 months------------------		
Cure Cycle	---------------1 hour @ 150 °C------------		

*Particulate elastomeric modifier from Hercules

EXAMPLE 18 - GLOB-TOP & DIE-ATTACH ADHESIVES
(Non Conductive)

BASE FORMULATIONS	Parts by Weight
ERL 4221E	50
Siloxy Monomer	35
Siloxy: CTBN adduct (50:50)	15
Irganox 1035	0.4

FINAL FORMULATIONS	A	B	C
Base	26.5	21	24
Wetting Agent (Pluronic L-101)	0.5	0.3	0.3
Silane A-187	0.5	0.7	0.7
Orasol Black CN	0.1	0.1	0.1
Silica FB-74FCS	32	77	72
Silica GP-3I	40	-	-
Iod. Catalyst (50% in 4221 E)	0.7	0.6	0.6
Copper Naphthenate (8% Cu)	0.02	0.02	0.02
Mercaptopropyltriethoxysilane (A-181)	1.0	1.0	-
D.C. 4-7051*	-	-	2

	A	B	C
Viscosity @ 25 °C, cps	45,000	65,000	38,000
Gel Time @ 120 °C	3-5 mins		
Shelf Life @ 25 °C	14 days		
@ -40 °C	> 6 months		
Cure Cycle	1 hour @ 150 °C		

*Particulate elastomeric modifier from Dow-Corning

EXAMPLE 19 - POLYMER-BUMP & SOLDER BALL REPLACEMENTS

BASE FORMULATIONS	Parts by Weight
ERL 4221E	50
Siloxy Monomer	35
Siloxy: CTBN adduct (50:50)	15
Irganox 1035	0.3

FINAL FORMULATIONS	A	B	C
Base	11	6	6
Wetting Agent (Pluronic L-101)	0.2	0.1	0.1
Silane A-187	0.3	0.2	0.2
Silverflake AAR-0595	88.2	--	--
Silflake 492	--	34	10
Silpowder SI-500*	--	60	84
Iod. Catalyst (50% in 4221E)	0.4	0.2	0.2
Copper Naphthenate (8% Cu)	0.01	0.01	0.01

Viscosity @ 25 °C, cps	54000	170000	44000
Gel Time @ 120 °C	----------2 mins------------------------------		
Shelf Life @ 25 °C	--------> 3 days----------------------------		
@ -40 °C	--------> 6 months-------------------------		
Cure Cycle	-----1 hour @ 150 °C-------------------- or -----1 hour @ 170 °C--------------------		
Cure Volatiles @ 150 °C	<0.1%	<0.05%	<0.05%
Volume Resistivity ohm-cm	6.4 x 10^{-5}	6.5 x 10^{-5}	3.2 x 10^{-5}

*25-35 micron spherical silver powder

EXAMPLE 20 - LOW STRESS ENCAPSULATIONS

	Parts by Weight	
BASE FORMULATIONS	A	B
ERL 4221E	40	20
Siloxy Monomer	40	40
Epiclon EXA-850 CPR*	-	20
Siloxy: CTBN adduct (50:50)	20	20
Irganox 1035	0.4	0.4
FINAL FORMULATIONS	A	B
Base	35	44
Wetting Agent (Pluronic L-101)	1	1
Silane A-187	0.5	0.5
Silane A-137	0.5	0.5
Mercaptopropyltriethoxysilane (A-1891)	1	0.5
Phthalo Blue Dispersion (2%)	0.5	0.5
PLV-65 (w/137)	60.2	51.6
Iod. Catalyst (50% in 4221E)	1.4	1.4
Copper Naphthenate (8% Cu)	0.03	0.035

	A	B
Viscosity @ 25 °C, cps	3,600	2,900
Gel Time @ 120 °C	---------6-8 mins-------	
Shelf Life @ 25 °C	--------> 7 days-------	
@ -40 °C	--------> 6 months----	
Cure Cycle	---1 hour @ 150 °C---	

*Low viscosity, ultra clean, low chlorine BPA epoxy resin

The foregoing results from testing compositions of the invention illustrate several major advantages over known die-attach, polymer bump, and encapsulant compositions. Attention is drawn to five significant parameters: (1) moisture absorption; (2) cure speed; (3) shelf life at room temperature (25°C); (4) weight loss during cure; and (5) thermal stability at higher temperatures (evidenced by low weight loss and no, or minimum loss of, adhesion at higher temperature). These parameters are of particular importance for die-attach, polymer bump, and encapsulant formulations because of the failures that commonly arise when devices incorporating known compositions are processed at elevated temperatures or are subsequently exposed to moisture.

The relationship of CTE to temperature is both important and subtle. When the CTE of the cured die-attach or encapsulant is significantly different from the CTE of the substrate and die, separation readily occurs on heating. A problem arises because the CTE of polymer-based die-attach adhesives and encapsulants undergoes a marked change at the T_g of the polymer. Thus, common polymers that might be otherwise useful, exhibit a CTE of 25-30 ppm below their T_g and 80-90 ppm above their T_g. Since their T_g's are commonly below 150°C, and the CTE of the substrate is about 15 ppm, severe constraints are presented on heating. The compositions of the invention, on the other hand, exhibit lower CTE's (20-25 ppm) that change very little below 200°C (40-50 ppm). This appears to be in part a result of the very high cross-linking of the polymers of the invention.

Also noteworthy is the very low moisture absorption (0.05-0.2%) of the inventive polymeric die-attach adhesives, polymer bumps, and encapsulants compared to the moisture absorption accepted as the industry standard (0.4-0.8%).

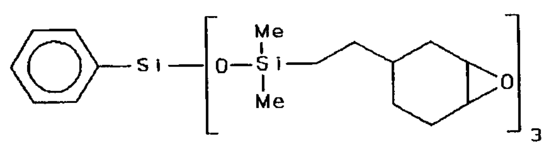
Finally, the lessened weight loss on curing (commonly 0.04% for the inventive compositions vs. a norm of 0.4-0.8%) and the minuscule weight loss of cured material on heating at 300°C (<0.1% for the inventive compositions vs. a norm of 0.4-0.6%) represent a remarkable improvement over compositions of the art.

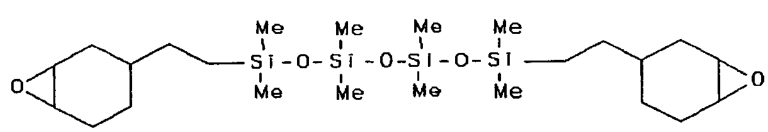
These advantages in the cured polymer are complemented by the unexpectedly superior shelf life of the uncured monomer formulation. The composition described in Example 8-1 has been found to exhibit less than 1000 cps change in viscosity on storage at room temperature for two weeks; indeed, such change as was observed was a decrease in viscosity. This is in marked contrast to one-component monomer formulations of the art, which increase in viscosity by several thousand cps over a few hours.

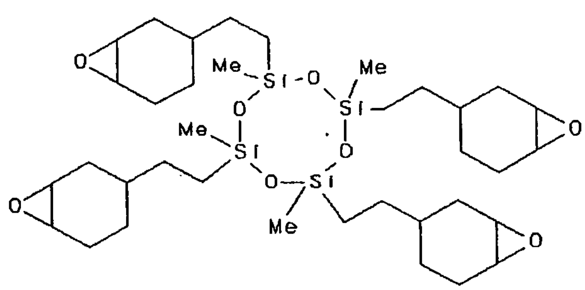
CLAIMS

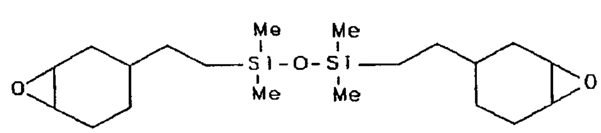
1. A resin composition comprising from about 5 to 100% by weight of a base resin and from about zero to 95% by weight of a particulate filler, wherein said base resin comprises:

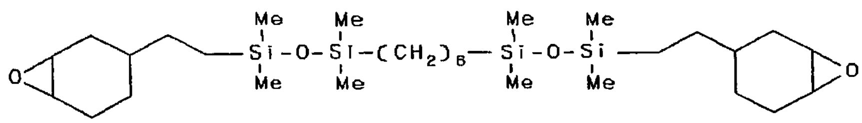
(a) from about 10 to 95 parts by weight of a cycloaliphatic epoxy functional siloxane selected from the group comprising

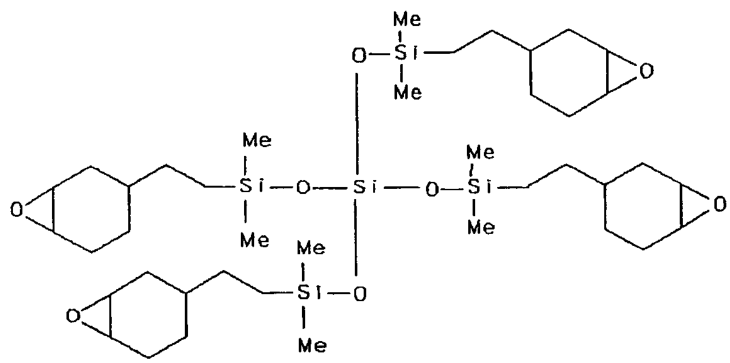






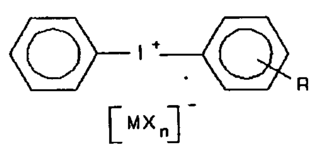






(b) from about 5 to 90 parts by weight of a non-silicon-containing di-, tri-, or polyepoxy resin or mixture of such resins;

(c) from about 0.1 to 3 parts by weight of an iodonium salt of formula



wherein M is selected from the group comprising boron, phosphorus, and antimony; X is halogen; n is 4 or 6; and R is selected from the group comprising hydrogen, C_1 to C_{20} alkyl, C_1 to C_{20} alkoxyl, C_1 to C_{20} hydroxyalkoxyl, halogen, and nitro; and

(d) from zero to about 3 parts by weight of a copper compound selected from the group comprising copper stearate, copper naphthenate, copper acetate, copper acetylacetonate, and copper 1,3-pentadienoate.

2. The resin composition according to claim 1 comprising from about 5 to 70% by weight of said base resin and from about 30 to 95% by weight of said particulate filler.

3. The resin composition according to claim 1, wherein said non-silicon-containing di-, tri-, or polyepoxy resin is a cycloaliphatic resin, a resin of a diglycidyl ether of bisphenol A, a resin of a diglycidyl ether of bisphenol F, a resin of a diglycidyl ether of brominated bisphenol A, an epoxidized vegetable oil resin, an epoxy cresol novolac, an epoxy phenol novolac, or an α-olefin epoxide.

4. The resin composition according to claim 3, wherein said cycloaliphatic resin is 3,4-epoxycyclohexyl-methyl 3',4'-epoxycyclohexane carboxylate, dicyclopentadiene dioxide, or bis(3,4-epoxycyclohexyl) adipate.

5. The resin composition according to claim 1, wherein said iodonium salt is [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate.

6. The resin composition according to claim 1, wherein said base resin additionally comprises from about 0.5 to 8 parts by weight of an

adhesion promoting agent selected from the group comprising glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, and mixtures thereof.

7. The resin composition according to claim 1, wherein said base resin additionally comprises from about 3 to 30 parts by weight of a toughener selected from the group comprising epoxidized polybutadiene, carboxyl-terminated polybutadiene, carboxyl-terminated polybutadiene acrylonitrile, and particulate elastomer fillers.

8. The resin composition according to claim 1, wherein said particulate filler is selected from the group comprising silver, gold, silica, quartz, alumina, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, boron nitride, carbon black, and diatomaceous earth.

9. The resin composition according to claim 1 comprising from about 5 to 40% by weight of said base resin and from about 60 to 95% by weight of said particulate filler selected from the group comprising silver, gold, silica, alumina, quartz, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride, wherein said base resin comprises:

(a) from about 20 to 45 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-

oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane;

(b) from about 40 to 60 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate;

(c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; and

(d) from zero to about 2 parts by weight of copper stearate or copper naphthenate;

and wherein said base resin additionally comprises:

(e) from about 0.4 to 3.5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and

(f) from about 5 to 20 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

10. The resin composition according to claim 1 comprising from about 5 to 40% by weight of said base resin and from about 60 to 95% by weight of said particulate filler selected from the group comprising silver and gold, wherein said base resin comprises:

(a) from about 20 to 50 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane;

(b) from about 30 to 60 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate;

(c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; and

(d) from zero to about 0.3 parts by weight of copper stearate or copper naphthenate;

and wherein said base resin additionally comprises:

(e) from about 1 to 5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and

(f) from about 5 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

11. The resin composition according to claim 1 comprising from about 30 to 50% by weight of said base resin and from about 50 to 80% by weight of said particulate filler selected from the group comprising silica, quartz, alumina,

aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride, wherein said base resin comprises:

(a) from about 30 to 70 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane;

(b) from about 20 to 65 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate;

(c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; and

(d) from zero to about 1.5 parts by weight of copper stearate or copper naphthenate;

and wherein said base resin additionally comprises:

(e) from about 1 to 8 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and

(f) from about 3 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

12. The resin composition according to claim 1 comprising from about 15 to 40% by weight of said base resin and from about 60 to 85% by weight of said particulate filler selected from the group comprising silica, quartz, alumina, aluminum nitride, aluminum nitride coated with silica, barium sulfate, alumina trihydrate, and boron nitride, wherein said base resin comprises:

(a) from about 20 to 50 parts by weight of 1,1,3,3-tetramethyl-1,3-bis[2-(7-oxabicyclo[4.1.0]hept-3-yl)ethyl] disiloxane;

(b) from about 30 to 70 parts by weight of 3,4-epoxycyclohexylmethyl 3',4'-epoxycyclohexane carboxylate and from zero to about 30 parts by weight of a diglycidyl ether of bisphenol A, a diglycidyl ether of bisphenol F, a diglycidyl ether of tetrabromo-bisphenol A, an epoxy cresol novolac, or an epoxy phenol novolac;

(c) from about 0.5 to 3 parts by weight of [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate; and

(d) from zero to about 1 part of copper stearate or copper naphthenate;

and wherein said base resin additionally comprises:

(e) from about 1 to 5 parts by weight of glycidoxypropyltrimethoxysilane, octyltriethoxysilane, mercaptopropyltriethoxysilane, or mixtures thereof; and

(f) from about 4 to 10 parts by weight of epoxidized polybutadiene, carboxyl-terminated polybutadiene, or carboxyl-terminated polybutadiene acrylonitrile.

13. A method for attaching a die to a substrate comprising:

(a) depositing a die-attach adhesive comprising a resin composition according to claim 1 on said substrate;

(b) positioning said die on said substrate in contact with said die-attach adhesive; and

(c) heating said substrate, die and die-attach adhesive at 110 to 200°C for 0.5 to 240 minutes.

14. The method according to claim 13, wherein said heating step (c) is performed at 130 to 150°C for 30 to 90 minutes.

15. The method according to claim 13, wherein said heating step (c) is performed at 150 to 160°C for 5 minutes to 1 hour.

16. The method according to claim 13, wherein said heating step (c) is performed at 160 to 180°C for 30 seconds to 5 minutes.

17. A method for reinforcing a solder bump connection or a polymer bump connection from a die to a substrate comprising:

(a) depositing an underfill encapsulant on the periphery of said die, wherein said die is connected to said substrate through said solder bump connection or said polymer bump connection and wherein said underfill encapsulant comprises a resin composition according to claim 1;

(b) allowing said deposited underfill encapsulant to contact said substrate, said die, and said solder or polymer bump connection; and

(c) heating said substrate, die and underfill encapsulant at 100 to 170°C for 5 to 240 minutes.

18. The method according to claim 17, wherein said heating step (c) is performed at 120 to 160° C for 15 to 180 minutes.

19. A method for protecting a die attached to a substrate comprising:

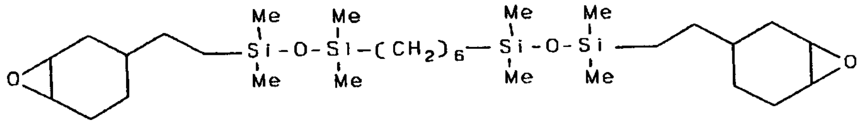
(a) depositing onto said die a glob-top encapsulant comprising a resin composition according to claim 1; and

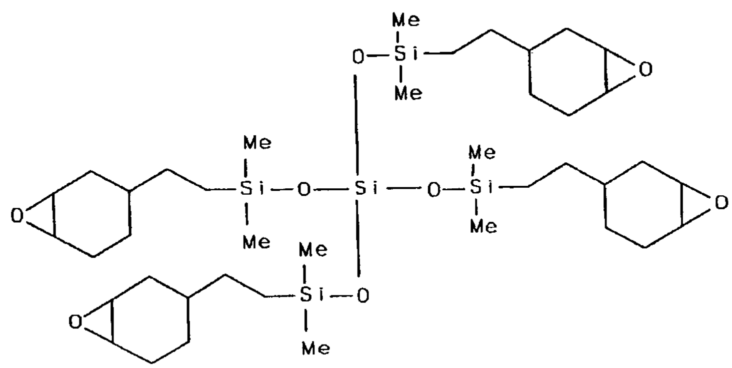
(b) heating said die and glob-top encapsulant at 100 to 170°C for 5 to 240 minutes.

20. The method according to claim 19, wherein said heating step (b) is performed at 120 to 160° C for 15 to 180 minutes.

AMENDED CLAIMS

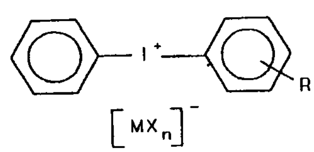
[received by the International Bureau on 24 December 1997 (24.12.97) original claims 1, 3 and 4 amended; remaining claims unchanged (2 pages)]





(b) from about 5 to 90 parts by weight of a non-silicon-containing di-, tri-, or polyepoxy resin or mixture of such resins;

(c) from about 0.1 to 3 parts by weight of an iodonium salt of formula



wherein M is selected from the group comprising boron, phosphorus, and antimony; X is halogen or C_6F_5; n is 4 or 6; and R is selected from the group comprising hydrogen, C_1 to C_{20} alkyl, C_1 to C_{20} alkoxyl, C_1 to C_{20} hydroxyalkoxyl, halogen, and nitro; and

(d) from zero to about 3 parts by weight of a copper compound selected from the group comprising copper stearate, copper naphthenate, copper acetate, copper acetylacetonate, and copper 1,3-pentadienoate.

2. The resin composition according to claim 1 comprising from about 5 to 70% by weight of said base resin and from about 30 to 95% by weight of said particulate filler.

3. The resin composition according to claim 1, wherein said non-silicon-containing di-, tri-, or polyepoxy resin is a cycloaliphatic epoxy resin, a resin of a diglycidyl ether of bisphenol A, a resin of a diglycidyl ether of bisphenol F, a resin of a diglycidyl ether of brominated bisphenol A, an epoxidized vegetable oil resin, an epoxy cresol novolac, an epoxy phenol novolac, or an α-olefin epoxide.

4. The resin composition according to claim 3, wherein said cycloaliphatic epoxy resin is 3,4-epoxycyclohexyl-methyl 3',4'-epoxycyclohexane carboxylate, dicyclopentadiene dioxide, or bis(3,4-epoxycyclohexyl) adipate.

5. The resin composition according to claim 1, wherein said iodonium salt is [4-(2-hydroxy-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate.

6. The resin composition according to claim 1, wherein said base resin additionally comprises from about 0.5 to 8 parts by weight of an

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/10528

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :156/330; 427/385.5, 386; 523/427, 434; 525/119, 122, 481, 525
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/330; 427/385.5, 386; 523/427, 434; 525/119, 122, 481, 525

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS, JPOABS, EPOABS, CAS ONLINE-Structure, Files Reg and CAPLUS, search terms: cycloaliphatic epoxides, epoxysiloxanes, iodonium

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 389,927 A2 (GENERAL ELECTRIC COMPANY) 3 October 1990, page 2, lines 46-52; page 4, lines 11-18 and page 5, Example 3.	1-12
Y	US 5,086,124 A (FUKUYAMA ET AL.) 04 February 1992, column 1, line 66 to column 2, line 23; column 6, lines 38-48 and column 9, Table 2, Examples 5 and 6.	1-12
Y	US 5,260,349 A (CRIVELLO) 09 November 1993, column 2, lines 44-45 and line 63 to column 3, line 29 and lines 42-46.	1-16
Y	US 5,073,643 A (CRIVELLO) 17 December 1991, column 3, lines 24-28; column 4, lines 11-24 and column 5, lines 14-15.	5 and 9-20

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 SEPTEMBER 1997	29 Oct 1997

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	ROBERT SELLERS
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,275,190 A (DUDGEON) 23 June 1981, column 1, lines 52-67; column 2, lines 35-37; column 3, lines 26-45.	7 and 9-20
Y	US 4,842,800 A (WALLES ET AL.) 27 June 1989, column 2, line 65 to column 3, line 8.	17-19

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/10528

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [ ] Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. [X] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
[ ] The additional search fees were accompanied by the applicant's protest.
[ ] No protest accompanied the payment of additional search fees.

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

B32B 15/06, 15/08, 27/04; CO8K 03/08, 03/22, 03/30, 03/34, 03/36, 03/38; CO8L 09/00, 09/02, 63/00, 63/02, 63/08; CO9J 109/00, 109/02, 113/00, 121/00, 163/00, 163/02, 163/04

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING
This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-6, 8 and 13-16, drawn to an epoxy-functional siloxane and polyepoxy resin composition and a method for attaching a die to a substrate.
Group II, claims 7 and 9-12, drawn to an epoxy-functional siloxane and polyepoxy resin composition further containing an epoxidized or carboxyl-terminated polybutadiene (acrylonitrile) toughener.
Group III, claims 7 and 9-12, drawn to an epoxy-functional siloxane and polyepoxy resin composition further containing particulate elastomer fillers.
Group IV, claims 17 and 18, drawn to an
epoxy-functional siloxane and polyepoxy resin composition and a method for reinforcing a solder bump.
Group V, claims 19 and 20, drawn to an epoxy-functional siloxane and polyepoxy resin composition and a method for protecting a die by encapsulation.

The inventions listed as Groups I-V do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

The resin compositions without the toughener of Groups I, IV and V are intermediates of the resin composition with the toughener of Groups II and III. The chemical structures of the intermediates of Groups I, IV and V and the final product of Groups II and III are unknown based on the diverse proportions and functionalities of the components. There is no evidence that the characteristic of the final product which is the inventive feature is due to the intermediate (PCT Administrative Instructions, Annex B, Part 1, section (g)(ii)(B)(iii) and Part 2, Examples 29 and 30).

The resin compositions of Groups II and III contain distint tougheners because the epoxy or carboxyl-functional polybutadiene (acrylonitrile) toughener of Group II does not share a common structure with the particulate elastomer filler of Group III. The former species is reactive with the epoxy-functional siloxane and polyepoxy resin and the latter species is non-functional, particulate and does not define any polybutadiene structure.

The die attachment of method of Group I, solder bump reinforcement of Group IV and die encapsulation of Group V are distinct methods involving mechanically different process steps which do not form a technical relationship.